257. *ω-Halogenomethyl-pyridines, -quinolines, and -*iso*quinolines. Part II.' Free-radical Reactions of ω-Halogenomethylquinolines.*

By B. R. Brown, J. O. Grice, D. Ll. Hammick, and B. H. Thewlis.

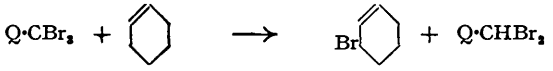
The indication that ωωω-tribromoquinaldine can undergo a free-radical dissociation (Waters and Robertson, *J.*, 1947, 492), $Q{\cdot}CBr_3 \rightleftharpoons Q{\cdot}CBr_2{\bullet} + Br{\bullet}$, has been confirmed by the observance of typical free-radical reactions with the side chains of substituted aromatic hydrocarbons, and of allylic substitution of *cyclo*hexene. ωω-Dibromoquinaldine undergoes these reactions at a higher temperature.

Waters and Robertson (*J.*, 1947, 492) suggested that " positive " halogen compounds react by way of a homolytic fission of the X–Hal bond. Their evidence is that such compounds (*e.g.*, *N*-bromosuccinimide and bromo-ketones) catalyse the autoxidation of tetralin, which is known to occur by way of a free-radical chain reaction. These workers found that ωωω-tribromoquinaldine catalyses the autoxidation, indicating that it is capable of undergoing a homolytic fission into free radicals. Further evidence for the participation of free radicals in the reactions of ωω-dibromo- and ωωω-tribromo-quinaldine is now presented.

ωωω-Tribromoquinaldine reacts with tetralin at 100° to yield ωω-dibromoquinaldine in 90% yield (Brown and Hammick, *J.*, 1950, 628). Similar reactions occur with xylene and with mesitylene, and it has been shown that about 70% of the bromine lost from the tribromo-compound appears in the aliphatic side chain of the hydrocarbon. This can only be interpreted as a free-radical reaction of the following type :

$$\begin{array}{rcl} Q{\cdot}CBr_3 & \rightleftharpoons & Q{\cdot}CBr_2{\bullet} + Br{\bullet} \\ R{\cdot}CH_3 + Br{\bullet} & \longrightarrow & R{\cdot}CH_2{\bullet} + HBr \\ R{\cdot}CH_2{\bullet} + Q{\cdot}CBr_3 & \longrightarrow & R{\cdot}CH_2Br + Q{\cdot}CBr_2{\bullet} \\ R{\cdot}CH_3 + Q{\cdot}CBr_2{\bullet} & \longrightarrow & R{\cdot}CH_2{\bullet} + Q{\cdot}CHBr_2\text{, etc.} \end{array}$$

The second of these reactions is preferred to $R{\cdot}CH_3 + Br{\bullet} \rightarrow R{\cdot}CH_2Br + H{\bullet}$ because free halogen atoms usually react with hydrocarbons by the abstraction of hydrogen and formation of a free hydrocarbon radical (Lu and Sugden, *J.*, 1939, 1273; Brown, Kharasch, and Chao, *J. Amer. Chem. Soc.*, 1940, **62**, 3435). Moreover, ωωω-tribromoquinaldine attacks the allylic position of *cyclo*hexene as does *N*-bromosuccinimide (Ziegler, Spath, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80) :



This is a typical free-radical reaction (Waters, *J.*, 1937, 2207; *Nature*, 1944, **154**, 772; Schmid and Karrer, *Helv. Chim. Acta*, 1946, **29**, 573). A similar mechanism is applicable to the disproportionation which occurs between ωωω-tribromoquinaldine and ω-monobromoquinaldine at 100° yielding ωω-dibromoquinaldine :

$$\begin{array}{rcl} Q{\cdot}CBr_3 & \rightleftharpoons & Q{\cdot}CBr_2{\bullet} + Br{\bullet} \\ Q{\cdot}CH_2Br + Br{\bullet} & \longrightarrow & Q{\cdot}CHBr{\bullet} + HBr \\ Q{\cdot}CHBr{\bullet} + Q{\cdot}CBr_3 & \longrightarrow & Q{\cdot}CHBr_2 + Q{\cdot}CBr_2{\bullet} \\ Q{\cdot}CH_2Br + Q{\cdot}CBr_2{\bullet} & \longrightarrow & Q{\cdot}CHBr_2 + Q{\cdot}CHBr{\bullet}\text{, etc.} \end{array}$$

At a temperature of 140° ωω-dibromoquinaldine undergoes similar reactions. Thus with tetralin, ω-monobromoquinaldine is formed, and a disproportionation between ωω-dibromoquinaldine and quinaldine yields ω-monobromoquinaldine. On account of the decreased crowding of the bromine atoms in ωω-dibromoquinaldine compared with ωωω-tribromoquinaldine, it is to be expected that a higher temperature will be necessary to cause appreciable free-radical dissociation: $Q{\cdot}CHBr_2 \rightleftharpoons Q{\cdot}CHBr\bullet + Br\bullet$.

EXPERIMENTAL.

Reaction of ωωω-Tribromoquinaldine with m-*Xylene and Mesitylene.*—A mixture of ωωω-tribromoquinaldine (10·0 g.) and *m*-xylene or mesitylene (200 ml.) was boiled under reflux for 2 hours. Steam-distillation from dilute (25% by vol.) sulphuric acid (to hold back the ωω-dibromoquinaldine) yielded a mixture of brominated *m*-xylenes and unchanged xylene, which were separated from the aqueous distillate and shaken with aqueous-alcoholic (50% by vol.) silver nitrate for 2 hours. The precipitated silver bromide was separated, washed with water and alcohol, dried at 120°, and weighed. With *m*-xylene, the average of eight runs for the percentage of side-chain bromination was 69; with mesitylene, the average was 75%.

Steam-distillation from alkaline solution after removal of the xylenes yielded ωω-dibromoquinaldine, m. p. and mixed m. p. 119°.

Reaction of ωωω-Tribromoquinaldine with cyclo*Hexene.*—*cyclo*Hexene (80 ml.) and ωωω-tribromoquinaldine (15 g.) were boiled under reflux until a test portion gave no reaction with acidified potassium iodide solution (3 hours). Distillation under reduced pressure gave a solid residue which on crystallisation from light petroleum yielded ωω-dibromoquinaldine (9·2 g., 78%), m. p. and mixed m. p. 119°. The distillate was fractionated to give 1-bromo*cyclo*hex-2-ene (3·8 g., 61%), b. p. 80—82°/40 mm. Ziegler *et al.* (*loc. cit.*) record b. p. 66—68°/35 mm.

Reaction of ωωω-Tribromoquinaldine with ω-Monobromoquinaldine.—ωωω-Tribromo- (1·9 g.) and ω-monobromo-quinaldine (1·1 g.) were heated at 100° for 1 hour. The melt was allowed to cool, and crystallised from light petroleum (b. p. 60—80°) to give ωω-dibromoquinaldine (1·25 g., 42%), m. p. and mixed m. p. 119°.

Thermolysis of ωω-Dibromoquinaldine in Tetralin.—ωω-Dibromoquinaldine (2·5 g.) was dissolved in redistilled tetralin (15 ml.), and heated at 145—150° for 2 hours. The liquid was cooled and shaken with dilute hydrochloric acid. The aqueous extract was shaken with chloroform (to remove traces of tetralin), made alkaline, and extracted with ether. Evaporation of the ether yielded a residue which was crystallised from light petroleum (b. p. 60—80°) to give ω-monobromoquinaldine (1·1 g., 59%) as colourless needles, m. p. and mixed m. p. 56·5°.

Reaction of ωω-Dibromoquinaldine with Quinaldine.—A mixture of ωω-dibromoquinaldine (1·5 g.) and redistilled quinaldine (0·7 ml.) was heated at 145—150° for 2 hours. The mixture was cooled and crystallised from light petroleum (b. p. 60—80°) to give ω-monobromoquinaldine (1·1 g., 50%), m. p. and mixed m. p. 56·5°.

DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

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